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Dielectric dispersion and relaxation studies of some pure nicotinates and their ternary mixtures at a single microwave frequency and temperature 36.5°C

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Abstract : Experimental values of dielectric parameters like $\varepsilon_s, \varepsilon_\infty, \varepsilon', \varepsilon''$, $\tau_{(0)}, \tau_{(1)}, \tau_{(2)}, \mu_D(s), \mu_0(s), \mu_D$ (microwaves) and α for four pure nicotinates namely benzyl nicotinate (BN), ethyl isonicotinate (EIN), methyl isonicotinate (MIN) and ethyl nicotinate (EN) and their ternary mixture compositions of the ternary systems (BN+MIN+EN) and (BN+EIN+EN) have been determined at a single microwave frequency 10.17 GHz and temperature 36.5°C. The compounds under investigation have been used in pure liquid from as dielectric samples. The most probable relaxation time $\tau_{(0)}$ is determined using Frohlich's equation. The experimental values of $\tau_{(0)}$ for ten ternary mixture compositions are compared with those calculated by different theoretical relations.

Keywords : Dielectric dispersion, dielectric parameters, relaxation time, molecular interactions

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1. Introduction

Although at microwave frequencies the dielectric relaxation studies of polar liquids in dilute solutions in nonpolar solvents reported earlier by many workers [1–3] provide sufficient information about intermolecular and intramolecular interactions but solute-solvent interactions in addition to solute-solute interactions make the study complex. The dilute solution method is lengthy and tiring and is unable to provide precise values of dielectric parameters for pure liquids alone but gives values for mixtures of polar liquids in non-polar liquids.

The study of dielectric behaviour of polar liquids in pure from provide us much information about the role of internal fields acting inside the dielectric sample. This method is straight

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forward, simple and produces more accurate information about intermolecular and intramolecular forces inside the experimental liquids. A few workers [4–7] have tried to investigate some pure polar liquids but a very little amount of work on higher order compositions have been reported so far. In the present paper dielectric relaxation behaviour of four pure polar liquids namely benzyl nicotinate, ethyl isonicotinate, methyl isonicotinate and ethyl nicotinate and their ten ternary mixture compositions in pure liquid state is investigated taking two systems of mixtures.

Four pure nicotinates and their five ternary mixture compositions of system No. 1 (BN+MIN+EN) and five other ternary mixture compositions of system No. 2 (BN+EIN+EN) in their pure from have been used as dielectric samples. The orientation of the molecules affected by the reaction field of the dipoles produces internal field effect within the dielectric sample. Therefore, the relaxation must occur by a group of molecules rather than a single molecule. Thus, we observe a macroscopic relaxation time which must be corrected to give a microscopic relaxation time. Although, various theories are available to determine the macroscopic relaxation time $\tau_{(0)}$ but Frohlich's theory provide sufficiently accurate results in case of pure liquids. The interpretation of the dielectric data have been used to understand the intermolecular and intramolecular interactions.

2. Experimental details

The experimental set-up, theory and procedure employed for the present investigation is described earlier [8]. The similar procedure is used here to determine various dielectric parameters like dielectric constant ε', dielectric loss ε'', dipole moment μ and relaxation behaviour of pure and ternary mixtures at microwave frequency 10.17 GHz and temperature 36.5°C. The accuracy of measurements for ε' and ε'' values is 1 to 5 percent. The static permittivity ε_s and optical permittivity ε_∞ for the samples under investigation have been measured with the help of a Toshniwal RL-09 type dipolemeter and Abbe's refractometer respectively. The compounds under investigation are of A.R. grade and are obtained from M/s Fluka A.G. Switzerland and have been used as such without any further purification.

Five ternary mixture compositions of system No. 1 (BN+MIN+EN) and another five ternary mixture compositions of system No. 2 (BN+EIN+EN) have been prepared by mixing of pure liquids namley benzyl nicotinate, methyl isonicotinate, ethyl nicotinate and ethyl isonicotinate in different proportions by weight.The corresponding mole fraction of components have been calculated by using usual relation for mixtures as described earlier in the literature [8,9].

The experimental values of ε' and ε'' for four pure nicotinates as well as their ternary mixture compositions at microwave frequency 10.17 GHz and temperature 36.5°C are obtained using the following relations :

$$\varepsilon' = (\lambda_0/\lambda_c)^2 + (\lambda_0/\lambda_d)^2 \left[1-(\alpha_d/\beta_d)^2\right] \quad (1)$$

$$\varepsilon'' = 2(\lambda_0/\lambda_d)^2\,(\alpha_d/\beta_d) \tag{2}$$

where α_d is the attenuation constant and $\beta_d = 2\pi/\lambda_d$ is the phase shift introduced per unit length of the sample. λ_0, λ_c and λ_d are the free space wave length, cutt-off wave length and the wave length in the dielectric medium respectively.

The most probable relaxation time $\tau_{(0)}$ have been determined experimentally by using Debye's equation derived by Frohlich. The other two relaxation times $\tau_{(1)}$ and $\tau_{(2)}$ are obtained by using an established Higasi *et al* [10] method by taking $\varepsilon_s, \varepsilon_\infty, \varepsilon', \varepsilon''$ values in place of slope values a_s, a_∞, a' and a'', in dilute solution method [8,9] The experimental values of relaxation times $\tau_{(1)}, \tau_{(2)}$ and $\tau_{(0)}$ are obtained using the following equations (3), (4) and (5).

$$\tau_{(1)} = (1/\omega)\left[\varepsilon''\,(\varepsilon' - \varepsilon_\infty)\right] \tag{3}$$

$$\tau_{(2)} = (1/\omega)\left[(\varepsilon_s - \varepsilon')\,\varepsilon''\right] \tag{4}$$

$$\tau_{(0)} = (1/\omega)\left[(\varepsilon_s - \varepsilon')/\varepsilon' - \varepsilon_\infty\right]^{1/2} = \left(\tau_{(1)} \times \tau_{(2)}\right)^{1/2} \tag{5}$$

where ω is the angular frequency of the wave.

The most probable relaxation time $\tau_{(0)mix}$ for mixture composition has been calculated using three theoretical methods namely simple mixing rule, reciprocal mixing rule and the method developed by Yadav and Gandhi [11], respectively given as under .

S.M. Rule
$$\tau_{(0)mix} = \sum_{i=1}^{3} x_i\,\tau_{(0)i} \tag{6}$$

R M. Rule
$$1/\tau_{(0)mix} = \sum_{i=1}^{3}\left(x_i/\tau_{(0)i}\right) \tag{7}$$

Y & G Method
$$\tau_{(0)mix} = \sum_{i=1}^{3}\left(X_i\tau_{(0)i}^2\right)\Big/\sum_{i-1}^{3} X_i \tag{8}$$

where
$$\left.\begin{aligned} X_1 &= x_1/(\varepsilon_2' - \varepsilon_{\infty 2})(\varepsilon_3' - \varepsilon_{\infty 3}) \\ X_2 &= x_2/(\varepsilon_1' - \varepsilon_{\infty 1})(\varepsilon_3' - \varepsilon_{\infty 3}) \\ X_3 &= x_3/(\varepsilon_1' - \varepsilon_{\infty 1})(\varepsilon_2' - \varepsilon_{\infty 2}) \end{aligned}\right] \tag{9}$$

Here $x_{i=1,2,3}$ are mole fractions of individual components of the mixture compositions.

The dipole moment values $\mu_D(s)$ and $\mu_0(s)$ at static low frequencies have been calculated by using Debye's and Onsagar's equations (10) and (11) respectively.

$$\mu_D^2(s) = (9kTM/4\pi Nd)\left[(\varepsilon_s - 1)/(\varepsilon_s + 2) - (\varepsilon_\infty - 1)/(\varepsilon_\infty + 2)\right] \tag{10}$$

$$\mu_0(s) = (9kTM/4\pi Nd)\left[\left((\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)\right)/\varepsilon_s(\varepsilon_\infty + 2)^2\right] \tag{11}$$

where M and d are the molecular weight and density of the polar liquid respectively.

The dipole moment $\mu_D(m)$ values at microwave frequency has been determined by using Debye's equation (12) given as under :

$$\mu_D^2(m) = (27kTM/4\pi Nd)\left[\varepsilon''/(\varepsilon_s + 2)(\varepsilon_\alpha + 2)\right]\left[\left(1 + \omega^2\tau^2\right)/\omega\tau_0\right] \tag{12}$$

where all symbols have their usual meanings. τ and $\tau_{(0)}$ are the microscopic and macroscopic relaxation times respectively which are related as

$$\tau = \left[(\varepsilon_\infty + 2)/(\varepsilon_s + 2)\right]\tau_0 . \tag{13}$$

The molecular weight M and density d of the mixture compositions used for the calculation of dipole moment are determined by using simple mixing rule of molecular weights and densities by using the relation (14) and (15) respectively.

$$M_m = \sum_{i=1}^{n} x_i M_i \tag{14}$$

$$d_m = \sum_{i=1}^{n} x_i d_i . \tag{15}$$

The distribution parameter (α) of the relaxation processes are determined using the following cole-cole arc equations (16) and (17).

$$\alpha = 1 - (2/\pi)\tan^{-1}(A/B) \tag{16}$$

where $A = \varepsilon''(\varepsilon_s - \varepsilon_\infty)$

$$B = (\varepsilon_s - \varepsilon')\ (\varepsilon' - \varepsilon_\infty) - \varepsilon''^2 \tag{17}$$

3. Results and discussions

The experimental values of dielectric parameters like $\varepsilon_s, \varepsilon_\infty, \varepsilon', \varepsilon'', \tau_{(0)}, \tau_{(1)}, \tau_{(2)}, \mu_D(s), \mu_0(s), \mu_D$ (microwaves) and α for pure nicotinates and their ternary mixture composition are listed in Table 1.

The experimental values of $\varepsilon_{sm}, \varepsilon_{\infty m}, \varepsilon'_m$ and ε''_m for all mixture compositions are compared with those calculated theoretically by using the simple mixing rule of permittivities in Table 2.

A comparison has been made between experimental values of $\tau_{(0)}$ and theoretically calculated values by three theoretical methods in Table 3.

An examination of Table 1 for dipole moment (μ) values shows that ethyl nicotinate (EN) has the highest value of dipole moment while benzyl nicotinate (BN) has the lowest value of μ and ethyl isonicotinate (EIN) and methyl isonicotinate (MIN) have moderate values of dipole moment. The lowest value of dipole moment of benzyl nicotinate (BN) is probably due to the steric hinderance of benzyl moiety of ester causing an association with nitrogen containing benzene ring *i.e.* pyridine. The heighest value of μ of the ethyl nicotinate (EN) is on account of electronegative ester group and electronegative nitrogen which occupy meta positions to each other *i.e.* nearer in space in comparison to para isomer. The moderate values of μ of methyl isonicotinate (MIN) and ethyl isonicotinate (EIN) are because of the ester group and nitrogen occupying para positions with respect to each other. The slight lower value of μ of the later is again due to the steric effect of the ethyl group in the ester. This indicates that the ethyl nicotinate and methyl isonicotinate have significant contributions towards intermolecular and intramolecular interactions and ethyl isonicotinate has comparatively lower contribution. Benzyl nicotinate has the lowest contribution towards intermolecular and intramolecular interactions in the mixture compositions, depending upon the change in molecular environments, shape and size of molecules.

Further examination of μ values shows that the experimental values of $\mu_D(s)$ at static frequency for the pure nicotinates as well as for ternary mixture compositions obtained from Debye formula are found lower than those values of $\mu_D(s)$ calculated by Onsager's formula. This is due to the fact that in the Onsager's formula due considerations have been given to the presence of internal fields while internal fields have been completely neglected in Debye's formula. Therefore, the dipole moment values calculated by Onsager and Debey's formulae follow the similar trend as reported by Singh [12] in case of pure liquids (Lutidines). These results are in good agreement with those obtained using dilute solutions method.

The higher deviations between experimental values of μ obtained by Debye and Onsagar's formulae are expected because intermolecular interactions in polar liquids produces deviation from the simple conditions envisaged by Debye whose version of

internal fields is now seriously in error. The more satisfactory representation of molecular dipole moment in non-associated liquids like EIN, MIN and EN is given by Onsager's equation. For associated liquids like BN, Frohlich and Kirkwood treatments are more appropriate but requires a detailed knowledge of liquid structure. Very low experimental values of μ for pure nicotinates at microwave frequencies may be expected because of a large change in intermolecular and intramolecular interactions occur inside the sample at these frequencies.

It is evident from Table 1 that among four pure nicotinates, ethyl nicotinate has the highest values of dielectric paramers $\varepsilon_s, \varepsilon_\infty, \varepsilon'$ and ε'' while benzyl nicotinate has the lowest values of the same parameters. This is reasonable because the same trend is obtained in μ values of the same samples. Therefore, in the mixture compositions of nicotinates ethyl nicotinate will have the highest contribution while benzyl nicotinate will have the lowest contribution towards these values.

Further, examination of Table 1 for ternary mixture system No.1 (BN+MIN+EN) reveals that $\varepsilon_s, \varepsilon_\infty, \varepsilon'$ and ε'' values does not show any systematic trend of change with the change in compositions of mixtures, which indicates the existence of association among the constituent molecules showing the presence of molecular interactions in the mixture compositions, causing a change in molecular environments in them. This is expected because of fact that one of the components of mixtures, namely the benzyl nicotinate has non-rigid associative molecules, while other two constituents of mixture composition (MIN) and (EN) have nonrigid and nonassociative molecules but there may be sufficient molecular interaction due to association of molecules of benzyl nicotinate with other molecules and non rigidity of all molecules create more molecular interactions.

It is obvious from Table 1 that ethyl nicotinate and methyl isonicotinate have considerable contribution towards ε' and ε'' values while benzyl nicotinate has the lowest contribution towards these values. This is again on expected lines discussed earlier.

Further examination of Table 1 reveals that the similar behaviour is observed in case of ternary system No.2 (BN+EIN+EN). This again confirms the highest contribution of ethyl nicotinate towards the same dielectric parameters for mixture compositions.

The comparison Table 2 shows that for all mixture compositions of system No.1 and system No. 2, the experimental values of ε_∞ and ε' are in good agreement with the theoretically calculated values. The percentage deviation between experimental and calculated values of ε_∞ and ε' is less than one percent and 3.14 percent respectively. The percentage deviations between experimental and calculated values of ε_s and ε'' are pretty high, in mixture compositions of both the systems. The higher deviations in ε_s values indicate that there are more changes in internal fields causing molecular interactions at low frequencies. The higher deviations in ε'' values cannot be explained by a single factor. There are many other factors like shape, size and environments of molecules in the mixture compositions which may be responsible for higher deviations and hence their effects should be considered.

Table 1. Experimentally determined dielectric parameters of four pure nicotinates and their ternary mixture compositions of Ternary system No 1 (BN+MIN+EN) and Ternary system No 2 (BN+EIN+EN) at temperature 36 5°C

Sl. No	Name of sample	Mr wt (M)	Density (d)					Relaxation time values			Dipole moment values			Distribution parameter
				ε_s	ε_∞	ε'	ε''	$\tau_{(0)} \times 10^{12}$ (Sec)	$\tau_{(1)} \times 10^{12}$ (Sec)	$\tau_{(2)} \times 10^{12}$	$\mu_D(s)$ (Debye)	$\mu_0(s)$ (Debye)	$\mu_D(m)$ (Debye)	(α)
1	Benzyl nicotinate	213 24	1 165	3 50	2 443	3 33	0 297	6 86	5 25	8 79	1 10	2 44	0 93	0 125
2	Ethyl isonicotinate	151	1 104	8 96	2 234	3 41	0 583	34 03	7 77	149 16	2 01	2 80	0 52	0 640
3	Methyl isonicotinate	137	1 160	19 25	2 272	3 63	0 619	51 13	7 14	395 29	2 28	4 28	0 29	0 703
4	Ethyl nicotinate	151	1 107	21 63	2 239	4 05	0 783	48 81	6 77	351 71	2 32	4 59	0 30	0 712
Ternary system No. 1 (BN+MIN+EN)														
5	T Mixture Comp No I (Mole fr of BN+ MIN+ EN 0 0254+ 0 7356+ 0 2390	142 12	1 148	17 99	2 268	3 80	0 5649	47 68	5 61	404 89	1 87	3 40	0 24	0 756
6	T Mixture Comp No II BN+ MIN+ EN 0 1414+ 0 6116+ 0 2470	151 34	1 148	6 30	2 296	3 68	0 531	21 55	6 01	77 29	1 50	1 85	0 57	0 640
7	T Mixture Comp No III BN+ MIN+ EN 0 4551+ 0 2598+ 0 2851	175 69	1 147	9 10	2 357	3 50	0 378	34 67	5 18	232 07	1 80	2 39	0 38	0 751
8	T Mixture Comp No IV BN+ MIN+ EN 0 4198+ 0 1243+ 0 4559	175 37	1 138	9 73	2 345	3 64	0 494	33 97	5 98	193 12	1 84	2 62	0 42	0 717
9	T Mixture Comp No V BN+ MIN+ EN 0 1608+ 0 1183+ 0 7209	159 36	1 123	13 16	2 286	3 93	0 601	37 12	5 73	240 58	1 90	3 05	0 35	0 736
Ternary System No. 2 (BN+EIN+EN)														
10	T Mixture Comp No 1 BN+ EIN+ EN 0 6778+ 0 0671+ 0 2551	193 19	1 146	7 70	2 391	3 49	0 438	30 66	6 24	150 57	1 79	2 42	0 49	0 693
11	T Mixture Comp No 2 BN+ EIN+ EN 0 5227+ 0 0595+ 0 4178	183 53	1 137	7 14	2 364	3 57	0 449	29 95	5 83	124 55	1 72	2 19	0 52	0 694
12	T Mixture Comp No 3 BN+ EIN+ EN 0 2796+ 0 0527+ 0 6677	168 40	1 123	12 74	2 309	3 84	0 576	37 77	5 89	242 04	1 94	3 06	0 21	0 730
13	T Mixture Comp No 4 BN+ EIN+ EN 0 0699+ 0 1586+ 0 7715	155 35	1 111	17 99	2 257	3 99	0 932	44 52	8 42	235 31	1 96	3 62	0 95	0 644
14	T Mixture Comp No 5 BN+ EIN+ EN 0 5835+ 0 2865+ 0 1300	187 32	1 140	4 06	2 372	3 44	0 565	11 94	8 29	17 99	1 27	1 39	0 96	0 230

Table 2. Comparison of experimental and theoretically calculated values of $\varepsilon_s, \varepsilon_\infty, \varepsilon'$ and ε'' for Ternary system No 1 (BN+MIN+EN) and Ternary system No 2 (BN+EIN+EN) at temperature 36 5°C

Sl No	Sample	ε_{sm} values			$\varepsilon_{\infty m}$ values			ε'_m values			ε''_m values		
		Exp	Calculated using S M rule	% deviation	Exp	Calculated using S M rule	% deviation	Exp	Calculated using S M rule	% deviation	Exp	Calculated using S M rule	% deviation
Ternary system No. 1 (BN+MIN+EN)													
1	T Mixture Comp No I BN+ MIN+ EN 0 0254+ 0 7356+ 0 2390	17 99	19 42	−7 95	2 268	2 269	−0 04	3 80	3 72	+2 11	0 549	0 650	−18 40
2	T Mixture Comp No II BN+ MIN+ EN 0 1414+ 0 6116+ 0 2470	6 30	17 61	−179 61	2 296	2 288	+0 35	3 68	3 69	−0 27	0 531	0 614	−15 63
3	T Mixture Comp No III BN+ MIN+ EN 0 4551+ 0 2598+ 0 2851	9 10	12 76	−40 22	2 345	2 340	+0 72	3 50	3 61	−3 14	0 378	0 519	−37 30
4	T Mixture Comp No IV BN+ MIN+ EN 0 4198+ 0 1243+ 0 4559	9 73	13 72	−41 01	2 345	2 329	+0 68	3 64	3 70	−1 65	0 494	0 559	−13 16
5	T Mixture Comp No V BN+ MIN+ EN 0 1608+ 0 1183+ 0 7209	13 16	18 43	−40 05	2 286	2 276	+0 44	3 93	3 88	+1 27	0 601	0 685	−13 98
Ternary system No. 2 (BN+EIN+EN)													
6	T Mixture Comp No 1 BN+ EIN+ EN 0 6778+ 0 0671+ 0 2551	7 70	8 49	−10 26	2 391	2 377	+0 59	3 49	3 52	−0 86	0 438	0 440	−0 46
7	T Mixture Comp No 2 BN+ EIN+ EN 0 5227+ 0 0595+ 0 4178	7 14	11 40	−59 66	2 364	2 345	+0 80	3 57	3 64	−1 96	0 449	0 517	−15 15
8	T Mixture Comp No 3 BN+ EIN+ EN 0 2796+ 0 0527+ 0 6677	12 74	15 89	−24 73	2 309	2 296	+0 56	3 84	3 82	+0 52	0 576	0 637	−10 59
9	T Mixture Comp No 4 BN+ EIN+ EN 0 0699+ 0 1586+ 0 7715	17 99	18 35	−2 00	2 257	2 2253	+0 18	3 99	3 90	+2 26	0 932	0 717	+23 07
10	T Mixture Comp No 5 BN+ EIN+ EN 0 5835+ 0 2865+ 0 1300	4 06	7 42	−82 76	2 372	2 357	+0 63	3 44	3 45	−0 29	0 565	0 442	+21 77

An examination of $\tau_{(0)}, \tau_{(1)}$ and $\tau_{(2)}$ values for four nicotinates as well as their ternary mixture compositions of both the systems listed in Table 1, shows that generally a large difference between $\tau_{(1)}$ and $\tau_{(2)}$ values exists for most of the samples indicating the presence of intramolecular interactions. This implies that the dielectric absorption by these molecules is not solely contributed by the rotation of molecules as a single unit, but intramolecular rotation also has a significant contribution towards the dielectric absorption. This concludes that all the molecules of pure components as well as mixture compositions under investigation relax by more than one relaxation process.

It is obvious from the largest difference between $\tau_{(1)}$ and $\tau_{(2)}$ values for methyl isonicotinate that it has the highest contribution towards intramolecular interactions in comparison to other three nicotinates. However, $\tau_{(0)}, \tau_{(1)}$ and $\tau_{(2)}$ values for benzyl nicotinate are of the same order. Perhaps, intramolecular interactions in it are either absent or very weak. In comparison to other three nicotinates, benzyl nicotinate has very small difference between its $\tau_{(1)}$ and $\tau_{(2)}$ values which may lead to very weak intramolecular interactions. Hence, this can be concluded that methyl isonicotinate and ethyl nicotinate have most significant contributions towards intramolecular interactions in mixture compositions and ethyl isonicotinate has a little lower contribution while benzyl nicotinate has very small contribution towards intramolecular interactions.

This is contrary to the general result that larger size molecules corresponds to higher values of relaxation time than that of the molecules of small size and volume. As benzyl nicotinate has molecules of largest size in comparison to the molecules of other three nicotinates, hence it should correspond to the biggest value of relaxation time but it has the lowest value of relaxation time. This may be explained as benzyl nicotinate has relatively small value of dipole moment. Therefore, it appears that inspite of its associative nature, the lower values of dipole moment of BN affects the relaxation time resulting into a lower value.

The sufficiently large difference between $\tau_{(1)}$ and $\tau_{(2)}$ values of ternary mixture composition of T. System No. 1 and No. 2 shows that these mixture compositions have significant contribution towards intramolecular interactions. However, the amount of contribution of such interactions towards relaxation properties is different in different compositions.

Further, examination of $\tau_{(0)}$ values shows that for all mixture compositions $\tau_{(0)}$ values lies between lowest and highest values of individual components. Such a behaviour of mixture compositions can possibly be explained by simple overlapping of three individual Debye regions. It is interesting to note here that $\tau_{(0)}$ values for most of the mixture compositions are different from the corresponding average values computed from $\tau_{(0)}$ values of individual components. It is reasonable to expect that the $\tau_{(0)}$ values of mixture compositions are likely to be different from the averaged values because of the change in the molecular environment and molecular size of the relaxing unit.

Table 3. Comparison of experimental and theoretically calculated values of $\tau_{(0)}$ by using various methods for Ternary system No 1 and Ternary system No 2 at temperature 36 5°c

Sl No	Sample	$\tau_{(0)} \times 10^{12}$ (Sec) experimental	$\tau_{(0)} \times 10^{12}$ (Sec) values calculated by using			Percentage deviation in $\tau_{0)}$ values by using		
			S M rule	R M rule	Y&G method	S M rule	R M rule	Y&G method
Ternary system No. 1 (BN+MIN+EN)								
1	T Mixture Comp No 1 | BN+ MIN+ EN | 0 0254+ 0 7356+ 0 2390 |	47 68	49 45	43 51	50 06	−3 71	+8 75	−4 99
2	T Mixture Comp No II | BN+ MIN+ EN | 0 1414+ 0 6116+ 0 2470 |	21 55	44 30	26 57	48 07	−105 57	−23 30	−123 06
3	T Mixture Comp No III | BN+ MIN+ EN | 0 4551+ 0 2598+ 0 2851 |	34 67	30 32	12 94	41 30	+12 55	+62 68	−19 12
4	T Mixture Comp No IV | BN+ MIN+ EN | 0 4198+ 0 1243+ 0 4559 |	33 97	31 49	13 71	42 13	+7 30	+59 64	−24 02
5	T Mixture Comp No V | BN+ MIN+ EN | 0 1608+ 0 1183+ 0 7209 |	37 12	42 34	24 68	46 89	−14 06	+33 51	−26 32
Ternary system No. 2 (BN+EIN+EN)								
6	T Mixture Comp No 1 | BN+ EIN+ EN | 0 6778+ 0 0671+ 0 2551 |	30 66	19 39	9 43	32 69	+36 76	+69 24	−6 62
7	T Mixture Comp No 2 | BN+ EIN+ EN | 0 5227+ 0 0595+ 0 4178 |	26 95	26 00	11 56	38 43	+3 53	+57 10	−42 60
8	T Mixture Comp No 3 | BN+ EIN+ EN | 0 2796+ 0 0527+ 0 6677 |	37 77	36 30	17 86	44 17	+3 89	+52 71	−16 95
9	T Mixture Comp No 4 | BN+ EIN+ EN | 0 0699+ 0 1586+ 0 7715 |	44 52	43 53	32 62	46 43	+2 22	+26 73	−4 29
10	T Mixture Comp No 5 | BN+ EIN+ EN | 0 5835+ 0 2865+ 0 1300 |	11 94	20 10	10 35	29 12	−68 34	+13 32	−143 87

An observation of distribution parameter (α) values shows that the individual components as well as all mixture compositions have finite values of (α) which are always less than unity. This observation, again confirms the two-relaxation processes in most of the samples. The lowest value of (α) for benzyl nicotinate in comparison to others leads to the existence of a single relaxation process in it and hence confirms a very small contribution towards intramolecular interactions.

Further, different mixture compositions have different values of α. This indicates that intramolecular interactions are different for different compositions. It is evident from the Table 1 that the α value for ethyl nicotinate is the highest. Ethyl isonicotinate and methyl isonicotinate have α values comparable to each other. However, α value for benzyl nicotinate is very small. This again support the significant contribution of ethyl nicotinate, ethyl isonicotinate and methyl isonicotinate towards strong intermolecular and intramolecular interactions in mixture compositions.

The comparison Table 3 for most probable relaxation time $\tau_{(0)}$ values shows that the percentage deviations between experimental and calculated values obtained by three theoretical methods are different for different compositions. The magnitudes of these deviations are pretty high. This indicates that the none of the theoretical methods provide results in fair agreement with the experimental results. In fact this type of behaviour can be explained as none of the theoretical methods has taken into account of the contribution by intermolecular and intramolecular interactions. All the theoretical methods are based on the consideration that molecules have simple structure and the internal fields do not change. But it is already mentioned here that the internal fields changes in mixture compositions with the change in compositions, which causes strong intermolecular and intramolecular interactions within the dielectric samples.

Inter comparison of three theoretical methods shows that the performance of the reciprocal mixing rule is slightly better than that of the other two methods. Hence, for prediction of accurate $\tau_{(0)}$ values of ternary as well as higher order systems, the theoretical relations should contain the terms representing intermolecular interactions between dissimilar molecules, variation in the internal fields, molecular structure and affinities among similar and dissimilar molecules.

It is obvious from Table 1, for most of the mixture compositions of system No. 2, the $\varepsilon', \varepsilon''$ and relaxation time values increases with increasing the mole concentration of ethyl nicotinate and ethyl isonicotinate in mixture compositions No. 1 to 4 and decreases in mixture composition No. 5. The lower values of dielectric parameters for mixture composition No. 5 is due to the fact that the maximum mole concentration of benzyl nicotinate is present in it. Hence, we may conclude that ethyl nicotinate and ethyl isonicotinate have significant contributions towards the dielectric parameters, representing the significant contribution towards intramolecular interactions, while benzyl nicotinate has much lower contribution.

In conclusion, we may say that the present study is quite useful in understanding the intermolecular and intramolecular interactions among the molecules of mixture compositions.

In the present investigations pure polar liquids are used directly as experimental samples which is convenient and straight forward in comparison to dilute solution method. However, it has a limitation that this method is suitable for highly polar liquids due to high absorption of e.m. power inside the dielectric samples. Though, enough care has been taken during the course of measurements but the precision of accuracy of measurements is within ± 1 to ± 5 percent

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